

**RAMAN SPECTROSCOPIC CHARACTERIZATION OF DIFFERENT TYPES OF PYROXENE.** A. WANG, B. L. JOLLIFF, K. M. VISKUPIC, AND L. A. HASKIN, Department of Earth & Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130. (alianw@levee.wustl.edu)

We have proposed Raman spectroscopy for on-surface mineralogical study of the Moon and Mars [1,2]. Pyroxenes are of particular interest. As a mineral class, they have a substantial range of structures and chemical compositions, and are frequently the key to deciphering rock petrogenesis. Determination of their compositional and structural characteristics in rocks and soils contributes greatly to understanding the petrologic processes that produced them. Raman spectroscopy is well suited for this determination.

During characterization of a lunar KREEP basalt fragment 15273,7039 [3], we analyzed the same spots on zoned pyroxene grains in a polished section by both Raman spectroscopy and electron microprobe analysis (EMPA). These grains cover a broad range of Fe, Mg, and Ca concentrations (Fig. 1). The grains range in Mg' (Mg/(Mg+Fe)) from magnesian orthopyroxene (Opx) with Mg' ~0.8 through pigeonite and augite at intermediate Mg' values to iron-rich clinopyroxene (Cpx) and pyroxferroite with Mg' <0.1, a range typical of lunar KREEP basalts [4]. Raman spectra and EMPA data were collected from 35 spots on these pyroxene and pyroxenoid grains. We observed a complex correlation between wavenumber positions of Raman peaks and cation ratios of the pyroxenes.

Figure 2 shows typical Raman spectra of Opx, Cpx, and triclinic pyroxferroite (a pyroxenoid, Pxnd [5]) in the fragment. Many peaks occur in each pyroxene spectrum; only the strongest of these are significant for analytical purposes. We call attention to five spectral regions; the spectra in all five regions are similar in pattern for all types of pyroxene, as follows: a strong asymmetric peak near 1000  $\text{cm}^{-1}$ , a strong doublet or an asymmetric single peak near 670  $\text{cm}^{-1}$ , a group of peaks in the 300-400  $\text{cm}^{-1}$  region, and two groups of weaker peaks near 500  $\text{cm}^{-1}$  and below 250  $\text{cm}^{-1}$ . We obtained precise positions of these peaks in four spectral regions of each Raman spectrum by curve fitting, using the Grams/386 curve-fitting program, with Gaussian-Laurentian mixed peak shape, linear baseline, and a free constraint calculation of all parameters (including the peak position, height, width, mixing percentage for each peak, and slope and intersection for baseline); results for each spectrum were iterated to convergence. The major individual peaks used for curve fitting are shown in the lowest spectrum of Fig. 2.

Exact peak positions in each of five spectral regions for different pyroxenes vary. Some variations are related to structural differences, and some depend on cation identity. An example of a structural effect is seen in the spectra of Opx and Cpx. Opx has a doublet in the

670  $\text{cm}^{-1}$  region because it has two types of pyroxene chains, each with a different bond length and bond angle. Cpx, in contrast, has only one type of chain and a single peak in the 670  $\text{cm}^{-1}$  region. Also, a peak lying higher than 230  $\text{cm}^{-1}$  in the region below 250  $\text{cm}^{-1}$  appears only in spectra of Opx. The effect of cation composition on peak position is shown in Figs. 3 and 4. The position of the peak near 1000  $\text{cm}^{-1}$  (Fig. 3a) shifts systematically as a function of cation composition. All pyroxferroite grains are Fe-rich; their spectra show the lowest peak positions in all five spectral regions, and only a single peak in 670  $\text{cm}^{-1}$  region. Where several peaks occur close together, apparent peak position can vary with crystal orientation, because excitation of a particular vibrational mode is favored by a particular angle between the crystal axis and the polarized laser beam.

In Figs. 3 and 4, Raman peak positions in two of the spectral regions are plotted as a function of Mg' and Wo content. Figures 3b and 4a show that peak frequencies in the 1000  $\text{cm}^{-1}$  and 670  $\text{cm}^{-1}$  regions decrease with increased Fe content. The points for Opx and Pxnd lie at the extremes of the curves. The correlations are evident despite an experimental problem; the pyroxene grains are zoned on a fine scale, so some differences in the sample volumes sensed by the two techniques adds an uncertainty to the match between the Raman and the EMP values.

The peak near 1000  $\text{cm}^{-1}$  arises from the symmetric stretching mode of  $\text{SiO}_4$  tetrahedra in the pyroxene chain; its frequency variation arises from the mass effect of the adjacent cations, and can thus be used to estimate Mg'. Similar peak shifts are known for the symmetric stretch mode in olivine [6]. The frequency of the small peak above 1010  $\text{cm}^{-1}$  shows no correlation with Mg' (Fig. 3a) or Wo content (not shown), but it correlates with structure (~1022  $\text{cm}^{-1}$  for Opx, ~1012  $\text{cm}^{-1}$  for Cpx); Figure 3a shows this gap. Triclinic pyroxenoid does not give this small peak. The peak near 670  $\text{cm}^{-1}$  arises from the symmetric vibration of Si-O<sub>b</sub>-Si bond that connects  $\text{SiO}_4$  groups in the pyroxene chain (O<sub>b</sub> = bridging oxygen). Its frequency depends on Si-O<sub>b</sub> bond length, the Si-O<sub>b</sub>-Si bond angle, and the cation at the M2 site. We thus see a correlation between this peak position and Wo content, as well as differences among the structural groups (Fig. 4b). The correlation (Fig. 4a) between this peak position and Mg' apparently stems mainly from M2 site substitution, because the coordination polyhedron of the M1 cation does not include bridging oxygens.

Fig. 1. Quadrilateral composition of pyroxene grains in KREEP basalt fragment 15273,7039. Fig. 2. Typical Raman spectra of pyroxene of three different structures. Fig. 3. Correlation of Raman peak positions near  $1000\text{ cm}^{-1}$  and  $\text{Mg}/(\text{Mg}+\text{Fe})$  ratio of pyroxene. Fig. 4. Correlation of Raman peak position near  $670\text{ cm}^{-1}$  and  $\text{Mg}/(\text{Mg}+\text{Fe})$ , Wo content in pyroxene.



**Fig. 4**

